

## Separation of Coal-Derived Liquids By Gel Permeation Chromatography

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### INTRODUCTION

Characterization and estimation of components in coal derived products are always time consuming and complex due to the number of various constituents present in them. Most of the people working in this area try to separate coal derived mixtures into four or five fractions and each fraction is enriched with chemically similar species (1 to 7). The fractionation is achieved by either using the difference in the solubility of various components in solvents with different chemical affinities or using absorption chromatography, mainly silica gel columns or various ion exchange and ion-pair columns. The latter achieves a cleaner separation than the former. The major disadvantage of both techniques is the loss of material balance at the end of the separation and the time consuming steps involved. Development of technology on hydro-genation and solvent liquefaction of coal requires analytical techniques for the fast reliable monitoring of coal derived fluids. When solvents like tetralin are used for the liquefaction experiments the analysis of the coal derived products is complex due to the large excess of tetralin and tetralin-derived products in the liquid phase of the system. The removal of the solvent system by conventional separation methods like distillation may result in the partial or complete loss of a number of coal-derived components with boiling points close to that of tetralin. This paper discusses the use of gel permeation chromatography followed by high resolution gas chromatography-mass spectrometry for the separation and characterization of coal derived liquids.

### GEL PERMEATION CHROMATOGRAPHY (GPC)

Gel Permeation Chromatography uses columns packed with swelled polymer particles with controlled pore size, formed by the copolymerization of styrene and divinylbenzene. GPC separates molecules according to molecular size based upon a distribution between a stationary phase of controlled pore size distribution and mobile liquid phase. Larger molecules elute faster than smaller molecules since larger molecules are less probable to diffuse into the liquid trapped inside the pore. Selecting the columns with proper pore size which varies from 100Å to 10<sup>6</sup>Å, the technique can be used to separate molecules over a wide range of molecular size, several million to less than 100 molecular weight. The retention volume  $V_r$  in a GPC is given by the following equation,

$$V_r = V_i + KV_p$$

where  $V_i$  is the column interstitial volume,  $V_p$  is the total pore volume and  $K$  is the partition coefficient, the ratio of the accessible pore volume to the total pore volume. All solutes elute between  $V_i$  and  $V_i + V_p$ . For Styragel columns the value of the ratio of  $V_i$  to  $V_p$  is in the order 1-1.3. Consequently the total number of peaks that can be separated on GPC is limited compared to other modes of LC. Relatively larger samples can be separated without sacrificing much of the resolution in about 20

to 40 minutes. Because of its operational simplicity, GPC lends itself as an efficient method for fractionating samples according to molecular size.

### EXPERIMENTAL

In the separation of coal derived liquid we used two separate GPC systems. One system consists of four 100 Å  $\mu$ Styragel columns and THF as the liquid phase, while the other system consists of two 100 Å  $\mu$ Styragel columns and toluene phase. Two refractometers (Waters Model R 401 and R404) and a UV detector were used for monitoring the effluents from the columns. A flow rate in the range of 0.75 to 1 ml was used for both systems. The samples were injected into the systems as pure liquids or as a concentrated solution. A sample size of about 250  $\mu$ l was injected into the column for the separation of coal-derived liquids. Samples from liquefaction experiments using tetralin as hydrogen donor solvent were injected into the columns after filtration using micropore filter without any dilution. Syn-Crude from the Pittsburgh Energy Center pilot plant was obtained as a very viscous material and it was dissolved in THF and injected as a 25% solution after two filtrations using micro-pore filters. Since THF is an excellent solvent for coal-derived liquids, samples were dissolved in THF and used in the GPC system with toluene as the mobile liquid phase. A number of compounds representing various chemical species in coal-derived liquids were obtained from commercial sources and these were used without purification for GPC retention volume studies. When both THF and toluene GPC systems are used for the separation of a coal-derived sample, the fractions from one system were concentrated before injecting into the second system. In certain cases, the samples were completely evaporated and redissolved in the solvent of the second system. Most of these sample manipulations were conducted under dry anaerobic condition. The final characterization of components in various GPC fractions were done using GC and GC-MS. The methodology is expalined in earlier works (8 to 12).

### RESULTS AND DISCUSSION

Resolution and percentage of recovery are the two main issues to be solved in order to achieve a successful separation of any complex mixture by chromatographic techniques. The percentage of recovery is very close to 100% for GPC systems using Styragel columns and carrier solvents such as THF and toluene. Figure 1 shows the effect of sample size on peak broadening. Four compounds - octadecane, tetradecane, phenol and tetralin - used in the study represent three major chemical species found in coal-derived products namely straight chain hydrocarbons, phenols and aromatics. The precipitation of octadecane from the mixture was prevented by adding THF (about 15%) to the prepared sample. The use of concentrated or undiluted samples does not affect the specific retention volumes or resolutions. When sample size was increased from a few milligrams to over a hundred milligrams the observed peak broadening was minimal. GPC of a sample with each component over 50 milligram showed unacceptable peak broadening. It was also found that when a sample contained a large amount of one component and other components are not in the over loading range, the resolution of the minor components were unaffected by the overloading effect of the large component.

When THF is used as the mobile liquid phase certain species can hydrogen bond with THF resulting in a larger molecular size and a lower retention volume. When nonpolar solvents like toluene are used the molecular size is more or less unaffected. The retention volume of several compounds in THF and toluene are listed in Tables I and II. The effect of solvent on specific retention volumes of various compounds are illustrated in Figure 2. It is interesting to note that rigid molecules like aromatics have smaller molecular sizes (larger retention volumes) compared to straight chain hydrocarbons of similar molecular weights (8). Phenol hydrogen bonds with THF (1 to 1 complex) resulting in a molecular size larger than a four ring aromatic hydrocarbon. Tetralin, naphthalene and toluene have the same molecular size. It could be inferred that the molecular size in a liquid phase gets a substantial contribution from the

flexible part of the molecules or the bonds with freedom of rotation. No molecular effect resulting from the solute-association with toluene was detected.

The retention volume of known compounds could be used as a guide to fractionate coal-derived liquids. Contrary to the general belief that coal-derived liquids are extremely complex and are formed of several thousands of compounds a simple concept that coal-derived liquids are simple and composed of four or five distinct chemical species such as alkanes, 'asphaltenes', phenols and aromatics was used for GPC separations. By a trial and error method, the technique of fractionating coal-derived liquids by GPC system using THF as the mobile liquid phase was perfected. Figure 3 shows the GPC of a sample from a Texas lignite liquefaction experiment using tetralin as the hydrogen-donor solvent. The sample has about 20% lignite-derived products and the rest composed of tetralin and tetralin-derived products such as naphthalene and decalin. The GPC separates the sample into five fractions. The first fraction is composed of colloidal carbons as well as high molecular weight species. Although the high molecular weight species are not completely characterized, the preliminary test shows that they are mainly of saturated hydrocarbon chains. The second fraction is composed of hydrocarbon chains as well as asphaltenes. Vacuum distillation separates saturated hydrocarbons from the non-volatile asphaltenes. The term asphaltenes is used for a spectra of compounds seen in the GPC with a wide molecular weight distribution but they are relatively non-volatile or decompose at high temperature so that their characterization by GC-MS or MS is so far unsuccessful. Using the elemental analysis of the asphaltene derived from West Virginia sub bituminous coal, can be expressed as  $(C_{14}H_{15}O_xN_yS_z)_n$ , where values of x, y and z are less than 1. NMR and IR spectra of the asphaltene fraction is similar to those published by other workers (1). The molecular weight distribution, as it is apparent from the GPC pattern resembles to reported values (5).

The aliphatic portion of fraction 2 and fractions 3, 4 and 5 were analyzed by GC-MS and the total ion gas chromatograms of these fractions are shown in figure 4. The peaks are identified in Tables III, IV and V. Since the separation of fractions were made on an arbitrary basis, slight overlapping of some species are expected. The aliphatic fraction is almost free of any phenols and aromatics. A portion of the lower members of alkanes such as dodecane and tridecane are present in the phenolic cut (fraction 3). Although the phenolic cut did not have any aromatics, some of the low molecular weight phenols overlap into the aromatic cut. The cut between the hydrogen donor system namely tetralin and the coal-derived aromatics encounters unavoidable overlapping due to the column overloading effect of the tetralin system, which composes almost 80% of the sample size. Any alkylated aromatic with the exception of toluene (same effective molecular size as naphthalene) has a retention volume lower than that of naphthalene and the overloading causes broadening of the peak resulting from tailing. As a result fairly good separation of aromatics from the tetralin system is obtained. Figure 4e shows the separation of tetralin system. GPC does not separate tetralin from naphthalene or other tetralin-derived products due to their close molecular sizes.

Coal derived liquids from a pilot plant were also separated by GPC followed GC-MS. Since they do not contain a large amount of any hydrogen donor solvent system as in the case of the bench scale experiments, the separation is less complex in appearance. As far as individual components are concerned there is lot of similarity in the general pattern of various coal-derived liquids. Figure 5a shows the GPC of Syn-Crude sample (Pittsburgh Energy Center pilot plant, derived from West Virginia sub-bituminous coal.) Figures 5 b to f show the GPC of the fractions. It could be concluded from these figures that the recovery of the sample injected into the columns is nearly 100%. The components in fraction 1 have a greater tendency for spreading than others.

When the GPC system using THF is used for the separation of coal derived liquids, the GC-MS of various fractions indicate reasonably good separations. But nonvolatile components could still overlap and escape GC-MS detection. If large molecular size aromatics which are nonvolatile are present in the coal-derived liquids, they may be

present in the phenolic fraction. Phenolic fractions of coal-derived liquids from experiments using tetralin contain two isomers of octahydrobinaphthyl (dimeric form of tetralin) as shown in Figure 3b. The phenolic fraction may have overlapping from the low molecular size asphaltene. Use of a GPC system with toluene as the mobile liquid phase could solve some of these problems. GPC separation of Syn-Crude using toluene is shown in Figure 6a. The fractions were further separated by a GPC system using THF. In the toluene system both phenols and aromatics have more or less similar molecular sizes due to the absence of any hydrogen bonding between the solvent and the coal-derived products. Fraction 3 is composed of phenols and aromatics and Figure 6d shows their separation by the GPC system using THF. It could be assumed that any fraction from the toluene-GPC system should split up in the THF-GPC system if that fraction contains both hydrogen bonding and non-hydrogen bonding species. As expected, all three fractions from Toluene-GPC show signs of spreading due to hydrogen bonding in THF. Ultimately a combined use of two systems using two different solvents such as THF and Toluene can achieve a superior separation for coal derived liquids.

#### CONCLUSIONS

The analytical techniques have to be developed further for the characterizations of asphaltene and nitrogen containing species. It is quite likely that the latter could be separated using appropriate solvent manipulations in the GPC systems. It was found that various coal-derived liquids have more or less similar components. Although Texas lignite varies in its BTU value as well as its ash content, a striking similarity in the composition of lignite-derived liquids was observed. Coal-derived liquids from West Virginia sub bituminous coal shows a resemblance to Texas lignite-derived liquids. The amount of aromatic species with three or more rings was detected in relatively small amounts. It could be quite possible that most coal may have a molecular structure made up of loosely bound building blocks such as alkylated phenols and alkylated aromatics (one or two ring-species predominating) and trapped long chain alkanes.

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Table I Retention Volume in THF

| <u>Compound</u>   | <u>Retention Vol.</u> |
|-------------------|-----------------------|
| Pyridine          | 34.7                  |
| Quinoline         | 33.08                 |
| Benzoquinoline    | 32.00                 |
| Acridine          | 32.00                 |
| N-Ethyl Carbazol  | 30.9                  |
| Aniline           | 30.26                 |
| Phenol            | 30.00                 |
| p-Cresol          | 29.3                  |
| Trimethyl phenol  | 29.0                  |
| $\beta$ -Naphthol | 28.64                 |
| Octanol           | 26.8                  |
| Tetradecane       | 25.0                  |

Table II Retention Volume in Toluene

| <u>Compound</u>  | <u>Retention Vol.</u> |
|------------------|-----------------------|
| Phenol           | 21.5                  |
| p-Cresol         | 19.7                  |
| Naphthol         | 19.7                  |
| Tetralin         | 18.97                 |
| Indol            | 17.91                 |
| Quinoline        | 16.66                 |
| Octanol          | 16.28                 |
| N-Ethyl Carbazol | 14.6                  |
| Tetradecane      | 14.0                  |
| Octadecane       | 11.66                 |

Table III Hydrocarbon Chains Separated from GPC Fraction #2

| <u>Aliphatic Fraction</u> |                        | <u>Aliphatic Fraction</u> |                 |
|---------------------------|------------------------|---------------------------|-----------------|
| <u>Retention Time</u>     |                        | <u>Retention Time</u>     |                 |
| <u>(Min.)</u>             | <u>Compound</u>        | <u>(Min.)</u>             | <u>Compound</u> |
| 8.0                       | Dodecane               | 33.5                      | Heneicosane     |
| 9.7                       | Tridecane              | 35.9                      | Docosane        |
| 13.7                      | Tetradecane            | 38.2                      | Tricosane       |
| 16.7                      | Pentadecane            | 40.4                      | Tetracosane     |
| 19.8                      | Hexadecane             | 42.7                      | Pentacosane     |
| 22.9                      | Heptadecane + Pristine | 44.8                      | Hexacosane      |
| 25.7                      | Octadecane             | 46.9                      | Heptacosane     |
| 28.3                      | Nonadecane             | 48.9                      | Octacosane      |
| 31.0                      | Eicosane               | 50.7                      | Nonacosane      |

Table IV Phenolic Fraction (GPC Fraction, #3)

| Retention Time<br>(min) | Compound                               | Retention Time<br>(min) | Compound   |
|-------------------------|--|-------------------------|--|
| 6.0                     | Phenol                                 | 36.9                    | n-Tetradecane $C_{14}H_{30}$ + $C_1$ -Alkylindanol |
| 7.4                     | n-Decane                               | 37.3                    | $C_5$ -Alkylphenol + $C_1$ -Alkylindanol           |
| 9.8                     | o-Cresol                               | 38.1                    | $C_5$ -Alkylphenol                                 |
| 11.2                    | p-Cresol + m-Cresol                    | 39.3                    | $C_5$ -Alkylphenol                                 |
| 12.9                    | n-Undecane                             | 40.7                    | $C_2$ -Indanol                                     |
| 14.9                    | $C_2$ -Alkylphenol                     | 42.4                    | Dimethyl Benzothiofene                             |
| 17.1                    | $C_2$ -Alkylphenol                     | 43.2                    | Dimethyl Indanol                                   |
| 18.2                    | $C_2$ -Alkylphenol                     | 43.7                    | n-pentadecane + $C_2$ -Alkylindanol                |
| 19.1                    | $C_2$ -Alkylphenol                     | 45.1                    | $C_2$ -Alkylindanol                                |
| 20.2                    | $C_3$ -Alkylphenol                     | 46.1                    | $C_2$ -Alkylindanol                                |
| 20.8                    | $C_3$ -Alkylphenol + n-Dodecane        | 47.2                    | $C_2$ -Alkylindanol                                |
| 21.9                    | $C_3$ -Alkylphenol                     | 48.0                    | $C_3$ -Alkylindanol                                |
| 23.0                    | $C_3$ -Alkylphenol                     | 48.9                    | $C_3$ -Alkylindanol                                |
| 23.7                    | $C_3$ -Alkylphenol                     | 50.0                    | $C_3$ -Alkylindanol + Hexadecane                   |
| 24.1                    | $C_3$ -Alkylphenol                     | 50.9                    | $C_3$ -Alkylindanol                                |
| 24.4                    | $C_3$ -Alkylphenol                     | 51.8                    | $C_3$ -Alkylindanol                                |
| 25.8                    | $C_3$ -Alkylphenol                     | 53.0                    | $C_1$ -AlkylNapththol                              |
| 26.7                    | $C_3$ -Alkylphenol                     | 54.1                    | $C_4$ -Alkylindanol + $C_1$ -AlkylNapththol        |
| 26.9                    | $C_3$ -Alkylphenol                     | 55.3                    | $C_1$ -AlkylNapththol                              |
| 28.1                    | $C_3$ -Alkylphenol                     | 56.3                    | $C_1$ -AlkylNapththol                              |
| 29.3                    | n-Tridecane                            | 57.5                    | $C_4$ -Alkylindanol                                |
| 30.0                    | $C_4$ -Alkylphenol                     | 59.9                    | Dimethyl Napththol                                 |
| 30.5                    | $C_4$ -Alkylphenol                     | 61.7                    | Dimethyl Napththol                                 |
| 31.3                    | $C_4$ -Alkylphenol                     | 62.7                    | Dimethyl Napththol                                 |
| 31.5                    | $C_4$ -Alkylphenol                     | 63.4                    | Dimethyl Napththol                                 |
| 33.5                    | $C_4$ -Alkylphenol + Indanol           |                         |  |
| 33.7                    | $C_4$ -Alkylphenol + $C_5$ Alkylphenol |                         |  |
| 34.1                    | $C_4$ -Alkylphenol + $C_5$ Alkylphenol | 81.2                    | Octahydro 2,2 Binaphthyl                           |
| 35.3                    | $C_5$ -Alkylphenol                     | 83.2                    | Octahydro, Binaphthyl                              |
| 36.2                    | $C_5$ -Alkylphenol                     |                         |  |

Table V Aromatic Fraction (GPC fraction #4)

| Retention Time<br>(min) | Compound                                    | Retention Time<br>(min) | Compound   |
|-------------------------|---|-------------------------|--|
| 6.1                     | Phenol                                      | 29.6                    | C <sub>3</sub> -Alkylindan                                       |
| 6.9                     | C <sub>3</sub> -Alkylbenzene + Phenol       | 30.0                    | C <sub>1</sub> -Alkyl-naphthalene                                |
| 8.9                     | C <sub>3</sub> -Alkylbenzene                | 30.7                    | C <sub>3</sub> -Alkylindan                                       |
| 10.1                    | o-Cresol                                    | 31.5                    | C <sub>3</sub> -Alkylindan + C <sub>4</sub> - Alkylindan         |
| 11.1                    | p-Cresol                                    | 31.9                    | C <sub>4</sub> -Alkylindan                                       |
| 11.9                    | m-Cresol                                    | 32.7                    | C <sub>4</sub> -Alkylindan                                       |
| 13.0                    | m-Cresol + C <sub>4</sub> - Alkylbenzene    | 33.7                    | C <sub>4</sub> -Alkylindan                                       |
| 13.7                    | C <sub>1</sub> -Alkylindan                  | 34.5                    | C <sub>2</sub> -Alkyl-naphthalene                                |
| 14.6                    | C <sub>2</sub> -Alkylphenol                 | 35.1                    | C <sub>4</sub> -Alkylindane + C <sub>2</sub> - Alkyl-naphthalene |
| 15.6                    | C <sub>2</sub> -Alkylphenol                 | 35.6                    | C <sub>4</sub> -Alkylindane                                      |
| 16.2                    | C <sub>2</sub> -Alkylphenol                 | 36.2                    | C <sub>5</sub> -Alkylindane + C <sub>2</sub> - Alkyl-naphthalene |
| 17.4                    | C <sub>2</sub> -Alkylphenol                 | 37.2                    | C <sub>3</sub> -Alkyl-naphthalene                                |
| 18.5                    | C <sub>1</sub> -Alkylindan                  | 37.6                    | C <sub>5</sub> -Alkylindan                                       |
| 20.8                    | Naphthalene                                 | 38.2                    | C <sub>5</sub> -Alkylindan + C <sub>3</sub> - Alkyl-naphthalene  |
| 21.4                    | Naphthalene + C <sub>5</sub> - Alkylbenzene | 38.4                    | C <sub>3</sub> -Alkyl-naphthalene                                |
| 21.9                    | C <sub>5</sub> -Alkylbenzene                | 39.5                    | C <sub>5</sub> -Alkylindan                                       |
| 22.5                    | C <sub>5</sub> -Alkylindan                  | 40.5                    | C <sub>3</sub> -Alkyl-naphthalene + C <sub>5</sub> - Alkylindan  |
| 22.9                    | C <sub>2</sub> -Alkylindan                  | 40.8                    | C <sub>3</sub> -Alkyl-naphthalene                                |
| 23.7                    | C <sub>5</sub> -Alkylbenzene                | 41.4                    | C <sub>3</sub> -Alkyl-naphthalene                                |
| 25.0                    | C <sub>2</sub> -Alkylindan                  | 41.7                    | C <sub>3</sub> -Alkyl-naphthalene                                |
| 25.7                    | C <sub>2</sub> -Alkylindan                  | 42.1                    | C <sub>3</sub> -Alkyl-naphthalene                                |
| 26.9                    | C <sub>2</sub> -Alkylindan                  | 42.9                    | C <sub>4</sub> -Alkyl-naphthalene                                |
| 27.3                    | C <sub>3</sub> -Alkylindan                  | 44.6                    | C <sub>5</sub> -Alkyl-naphthalene                                |
| 28.8                    | C <sub>1</sub> -Alkyl-naphthalene           |                         |  |

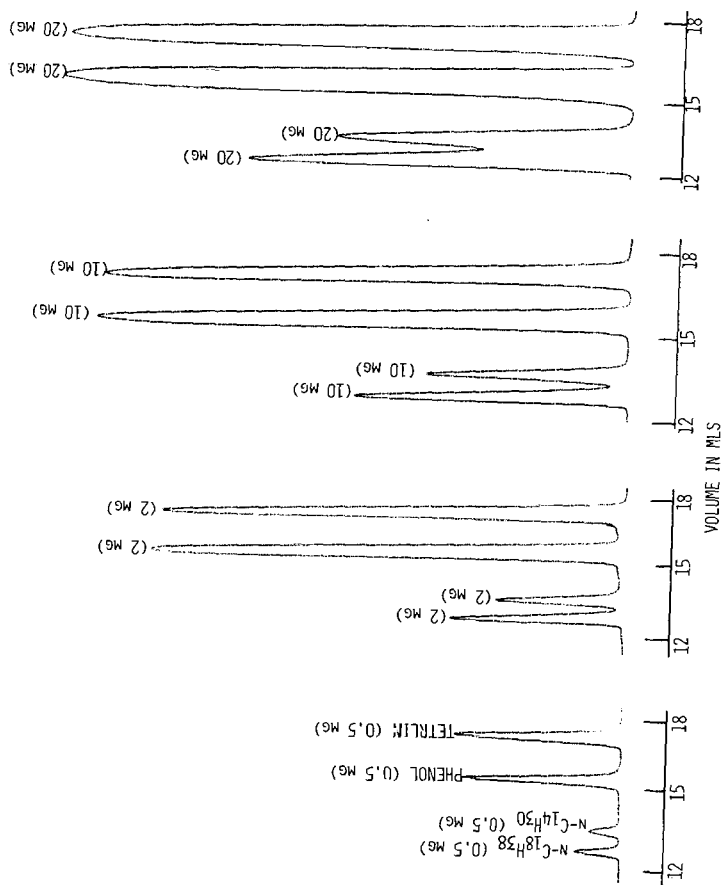


Figure 1. Effect of sample size on retention volume ( $V_r$ ) and resolution. GPC system used two  $\mu$ Styragel columns and THF as the liquid phase at a flow rate of 0.75 ml/min.

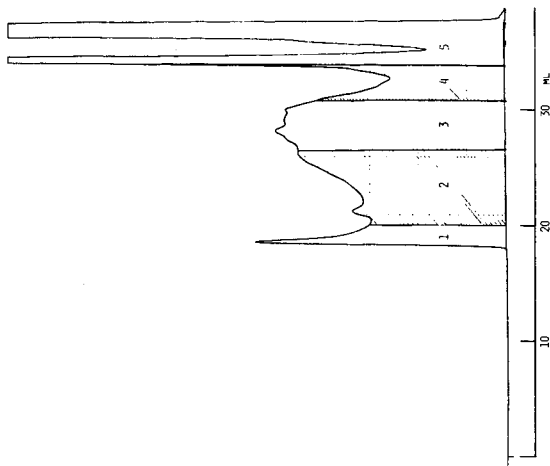
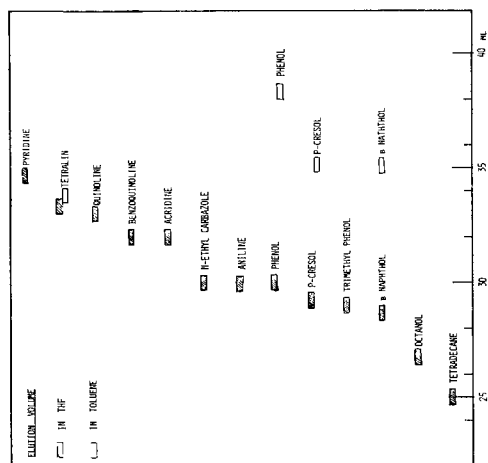


Figure 3. GPC separation of Texas lignite-derived products from liquefaction experiments using tetralin as a hydrogen-donor solvent. The GPC system consisted of 4 100 Å  $\mu$ Styragel columns and a THF flow rate of 1 mL/min. Fractions 2 through 5 were separated by GC-MS (Fig. 4a to d) and identified in Tables III through V.

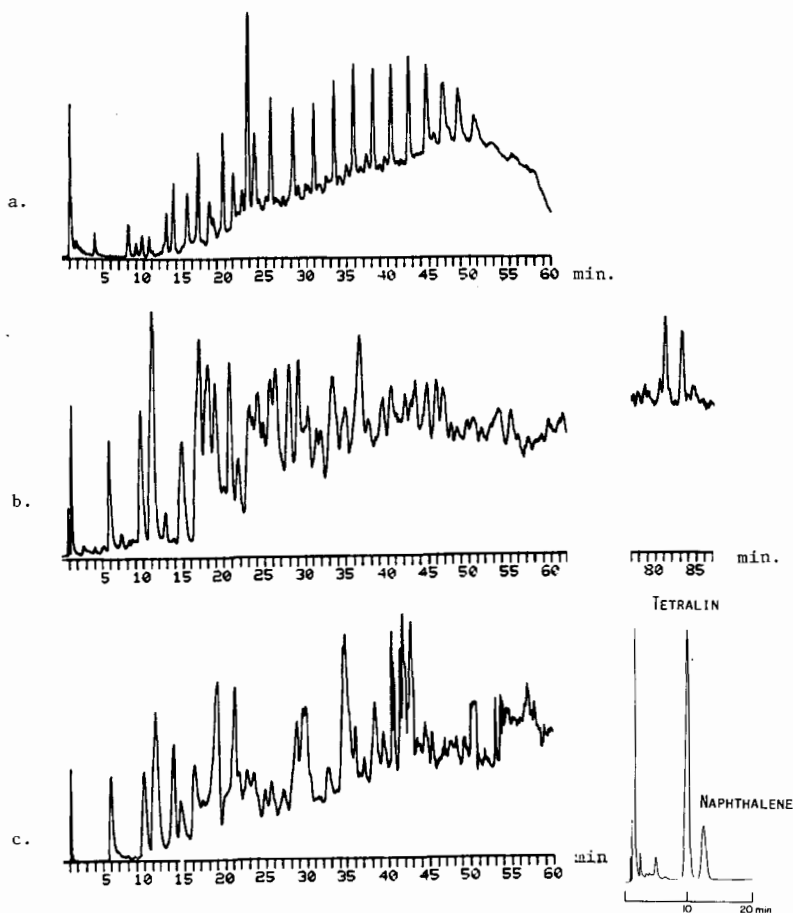


Figure 4. Total ion gas chromatogram of GPC fractions (Figure 3). Column: 5% Dexsil 300 on 100/120 Chromosorb H-WP, 1/8 in. od X 8 ft., carrier gas: 20 ml helium/min., a. Separation of hydrocarbon chains from GPC fraction #2, temperature program 80-270°C at 4 C/min. b. Separation of fraction #3, temperature program: 80-270°C at 2°C/min. for 40 min. followed by 4°C/min., c. Separation of fraction #4, temperature program 50°-270°C at 2°C/min. for 40 min. followed by 4°C/min. d. Fraction #5 was separated on a 10% SP2250 on 100/120 supelcoport 1/4 in. od X 8 ft. SS column at 160°C isothermal. Helium flow rate: 60 ml per min.

Figure 5a. Shows the separation of West Virginia sub bituminous coal-fluid by GPC using four 100 A  $\mu$ Styragel columns and a flow rate of 1 ml of THF/min. The fraction 1 to 4 reinjected into the same system after concentration and the GPC's of the fractions are shown in Fig. 5b to e in the order.

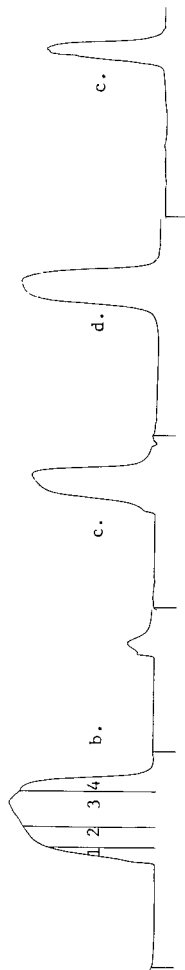


Fig. 5a.

Figure 6a. Shows the separation of West Virginia sub bituminous coal-derived fluid by GPC using 2 100 A  $\mu$ Styragel columns and a toluene flow rate of 0.75 ml per min. The fractions were evaporated and redissolved in THF and separated by GPC system using THF solvent (as in Figure 5). The GPC's of the fractions are shown in Fig. b to d in the order. The fractions contained small amounts of toluene.

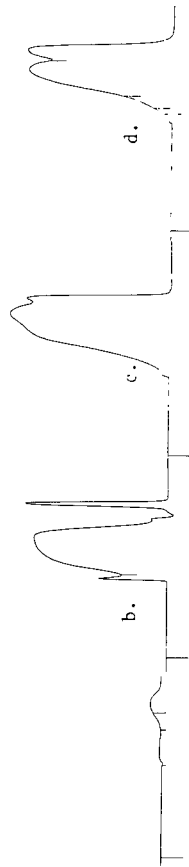


Fig. 6a.